

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN AND RELATING TO ELECTROCHEMICAL CELLS

(71) We, ENERGY CONVERSION LIMITED, a British Company of Britannic House, Moor Lane, London, E.C.2., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to electrochemical cells.

In the following specification and claims the term "start-up" means the time between first supplying oxidant or fuel to the system and when the system is producing its rated voltage. The term "shut-down" means the time between first shutting off the supply of oxidant or fuel to when all such supplies to the system are shut off.

According to one aspect of the invention there is provided an electrochemical cell system having a plurality of cells with an electrolyte common to all said cells and in which hydrogen is utilised as the fuel and oxygen or air is utilised as the oxidant, the system being such that the oxidant space of each cell is provided with a fluid, which is compatible with the electrodes and has substantially no free oxygen, whilst hydrogen is being supplied to the fuel space of each cell, during shut-down (as hereinbefore defined) and/or during start-up (as hereinbefore defined) of the system.

According to a further aspect of the invention there is provided a fuel cell system having a plurality of cells with all electrodes made of nickel and platinum, and an electrolyte common to all the cells, in which hydrogen is utilised as the fuel and oxygen or air is utilised as the oxidant, the system being such that the oxidant space of each cell is provided with a fluid, which is compatible with the electrodes and has substantially no free oxygen, whilst hydrogen is being supplied to the fuel space of each cell, during shut-down (as hereinbefore

defined) and/or during start-up (as hereinbefore defined) of the system.

The fluid may comprise a nitrogen atmosphere.

The nitrogen atmosphere may be provided by a supply which is utilised to purge the oxygen or air electrode spaces of each cell.

Alternatively, air is utilised as the oxidant and the nitrogen atmosphere is provided by not circulating air through the system during shut-down and/or start-up.

The fluid may comprise helium, argon, distilled water or an aqueous solution of potassium hydroxide.

According to yet a further aspect of the invention there is provided a method of operating an electrochemical cell system having a plurality of cells with an electrolyte common to said cells and in which hydrogen is utilised as the fuel and oxygen or air is utilised as the oxidant, comprising providing the oxidant space of each cell with a fluid, which is compatible with the electrodes and has substantially no free oxygen, whilst hydrogen is being supplied to the fuel space of each cell, during shut-down (as hereinbefore defined) and/or during start-up (as hereinbefore defined) of the system.

According to a still further aspect of the invention there is provided a method of operating a fuel cell system having a plurality of cells with all electrodes made of nickel and platinum, an electrolyte common to said cells and in which hydrogen is utilised as the fuel and oxygen or air is utilised as the oxidant, comprising providing the oxidant space of each cell with a fluid, which is compatible with the electrodes and has substantially no free oxygen, whilst hydrogen is being supplied to the fuel space of each cell, during shut-down (as hereinbefore defined) and/or during start-up (as hereinbefore defined) of the system.

Preferably air is used as the oxidant and the nitrogen atmosphere is produced by not circulating air through the system during shut-down and/or start up.

- 5 The system arrangement or method of operation is provided to prevent cell reversal during start-up and/or shut-down of the system.

- 10 In a particular fuel cell system the cell stack has a common electrolyte flowing in parallel through all the cells and the cells are electrically connected in series. It can be shown quite simply that under these conditions, internal "short circuit" currents will flow via the common electrolyte through all the cells in the stack. If any of the cells cannot support this current, because of reactant starvation, then the electrodes will polarise to a point where alternative electrode reactions take place.

- 15 With hydrogen as the fuel and air as the oxidant, the problem arises with the hydrogen electrode which when it is starved of hydrogen polarises to a reversed potential. 20 With cells with base electrolyte instead of hydrogen oxidation ($H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$) two alternative reactions can take place:—
(i) "Electrode" + $2OH^- \rightarrow$ "Electrode" oxide + $H_2O + 2e^-$

- 30 (ii) $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$
All the electrodes are constructed of platinum and nickel and can be oxidised to platinum oxide and/or nickel oxide. Platinum oxide is an extremely poor hydrogen catalyst whilst nickel oxide being a non-conductor could introduce a very high IR loss between the catalyst and the bulk current collector. In either case the polarisation of the electrode will be very severely increased.

- 40 Thermodynamically both oxides should be reduced by hydrogen, but at ambient temperatures the rate is extremely slow and it is believed that the rate is slower than the rate at which the oxides are electrochemically formed. The net result of the increased polarisation is that the electrodes cannot support the leakage currents even at open circuit and they stay permanently reversed; this is despite the electrodes subsequently having sufficient hydrogen.

- 50 At the present time for starting up a fuel cell system the electrolyte pump is switched on; this is an essential first step to ensure there is liquid between the porous electrodes to prevent hydrogen and air mixing. Next the air is turned on and the hydrogen circuit, including the anode compartments, is purged with nitrogen.
60 Finally the nitrogen is turned off and hydrogen fed to the cells.

- Since the hydrogen does not reach all the cells at the same time some cells develop a potential before others can support a current. The good cells can then cause an in-

ternal leakage current to flow through the common electrolyte and through all the cells. The cells with insufficient hydrogen are driven in reverse, with consequences previously described.

The cells then have to be de-reversed so that the cell stack can operate in the normal fashion.

On shut-down the hydrogen is purged with nitrogen and this purges some cells more quickly than others. Again some cells have a potential whilst others have insufficient hydrogen to support the leakage currents. By a similar mechanism cells are driven in reverse.

In accordance with one embodiment of the invention, the air compartments are purged with nitrogen before the hydrogen circuits then air electrodes can polarise in a similar manner to the hydrogen electrodes but this presents no problems of semi permanent cell reversal.

If on start-up nitrogen is on the air electrode when the nitrogen purge on the anode is switched to hydrogen no potential exists (H_2/N_2 cell has zero potential) and the hydrogen electrodes are not oxidised. When air is put into the cell stack some air electrodes will show temporary reversal until the nitrogen has been fully purged. When air is flowing freely through all the cells they will show their correct polarity.

On shut-down anode reversal is prevented again by bringing cell potentials to zero by purging the cathodes with nitrogen before purging off the hydrogen.

This method works well but does require extra nitrogen for purging both electrodes. This can be overcome in accordance with a further embodiment of the invention by, instead of purging with nitrogen, not circulating air during start-up or shut-down. In this case the remaining oxygen in the air in the air spaces is consumed by the leakage currents to leave a nitrogen atmosphere. When this is done on shut-down there will be a nitrogen atmosphere present for the next start-up. The success of this method depends to some extent on the volume of air stored in the air circuits and the rate of oxygen diffusion into the system during shut-down. In practice it has been found to work very well for shut-down periods of a few days and it also involves very little system complication.

In further embodiments of the invention the nitrogen may be replaced by a gas such as helium or argon or by a liquid such as distilled water or an aqueous solution of potassium hydroxide where this is the electrolyte being used. The criterion which determines whether a fluid is suitable is that it should have substantially no free oxygen.

Where electrolyte is used the air or oxygen sides of the cells are at least half

flooded and then the hydrogen sides can be flooded if required.

When the arrangement is utilised for a matrix type cell, or even free electrolyte cells, a small electrical load may be applied during such flooding which remains during start-up. This allows the anode electrodes to remain at a constant potential and the cathode electrodes rise to this potential so consuming all absorbed oxygen in the cells.

It will be noted that the invention is not merely applicable to systems having circulating electrolyte, but can be utilised to advantage in any system in which leakage currents occur, however small these may be.

WHAT WE CLAIM IS:—

1. An electrochemical cell system having a plurality of cells with an electrolyte common to all said cells and in which hydrogen is utilised as the fuel and oxygen or air is utilised as the oxidant, the system being such that the oxidant space of each cell is provided with a fluid, which is compatible with the electrodes and has substantially no free oxygen, whilst hydrogen is being supplied to the fuel space of each cell, during shut-down (as hereinbefore defined) and/or during start-up (as hereinbefore defined) of the system.

2. A fuel cell system having a plurality of cells with all electrodes made of nickel and platinum, and an electrolyte common to all the cells, in which hydrogen is utilised as the fuel and oxygen or air is utilised as the oxidant, the system being such that the oxidant space of each cell is provided with a fluid, which is compatible with the electrodes and has substantially no free oxygen, whilst hydrogen is being supplied to the fuel space of each cell, during shut-down (as hereinbefore defined) and/or during start-up (as hereinbefore defined) of the system.

3. A system as claimed in claim 1 or 2 wherein said fluid comprises a nitrogen atmosphere.

4. A system as claimed in claim 3 wherein the nitrogen atmosphere is provided by a supply which is utilised to purge the oxygen or air electrode spaces of each cell.

5. A system as claimed in claim 3 wherein air is utilised as the oxidant and the nitrogen atmosphere is provided by not circulating air through the system at shut-down and/or start-up.

6. A system as claimed in claim 1 or 2 wherein said fluid comprises helium.

7. A system as claimed in claim 1 or 2 wherein said fluid comprises argon.

8. A system as claimed in claim 1 or 2 wherein said fluid comprises distilled water.

9. A system as claimed in claim 1 or 2 wherein said fluid comprises an aqueous

solution of potassium hydroxide which constitutes the electrolyte of the system.

10. A system as claimed in claim 9 wherein the oxygen or air electrode portions are at least half flooded and then the hydrogen electrode portions are also flooded by the fluid.

11. A system as claimed in claim 10 which comprises a matrix type system, wherein a small electrical load is arranged to be maintained across the system during such flooding which remains during start-up.

12. A method of operating an electrochemical cell system having a plurality of cells with an electrolyte common to said cells and in which hydrogen is utilised as the fuel and oxygen or air is utilised as the oxidant, comprising providing the oxidant space of each cell with a fluid, which is compatible with the electrodes and has substantially no free oxygen, whilst hydrogen is being supplied to the fuel space of each cell, during shut-down (as hereinbefore defined) and/or during start-up (as hereinbefore defined) of the system.

13. A method of operating a fuel cell system having a plurality of cells with all electrodes made of nickel and platinum, an electrolyte common to said cells and in which hydrogen is utilised as the fuel and oxygen or air is utilised as the oxidant, comprising providing the oxidant space of each cell with a fluid, which is compatible with the electrodes and has substantially no free oxygen, whilst hydrogen is being supplied to the fuel space of each cell, during shut-down (as hereinbefore defined) and/or during start-up (as hereinbefore defined) of the system.

14. A method as claimed in claim 12 or 13 wherein said fluid comprises a nitrogen atmosphere.

15. A method as claimed in claim 14 wherein said nitrogen atmosphere is provided by a supply which is utilised to purge the oxygen or air electrode spaces of each cell.

16. A method as claimed in claim 14 wherein air is used as the oxidant and the nitrogen atmosphere is provided by not circulating air through the system at shut-down and/or start-up.

17. A method as claimed in claim 12 or 13 wherein the fluid comprises helium.

18. A method as claimed in claim 12 or 13 wherein the fluid comprises argon.

19. A method as claimed in claim 12 or 13 wherein the fluid comprises distilled water.

20. A method as claimed in claim 12 or 13 wherein the fluid comprises an aqueous solution of potassium hydroxide which constitutes the electrolyte of the system.

21. A method as claimed in claim 20

wherein the oxygen or air electrode spaces of each cell are at least half flooded and then the hydrogen electrode portions are also flooded by the fluid.

- 5 22. A method as claimed in claim 21 wherein a small electrical load is maintained across the system during such flooding which remains during start-up.

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